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Highly sensitive hydrogen gas sensors based on gold nanoparticle decorated zinc oxide nanosheets

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Abstract

Highly sensitive gold nanoparticle decorated zinc oxide nanosheet gas sensors have been fabricated using simple and rapid chemical methods capable of producing a normalised current gain of 2.54 (at 10V) in dry air containing 2.5ppm of hydrogen gas at 200C and a current gain of 382.53 under 125ppm. Compared to undecorated sheet based sensors where a response of 1.24 was observed under 125ppm at 200C a massive relative increase in signal is observed. The zinc oxide nanosheets are produced via a previously reported simple microwave assisted hydrothermal growth method and gold nanoparticles with mean diameter of 5nm synthesized via a simple sodium borohydride reduction of hydrogen tetrachloroaurate in the presence of polyvinylpyrrolidone (PVP) followed by drop casting onto a pre-patterned aluminium oxide substrate.

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Keywords:

1. Introduction

Detection and measurement of hydrogen concentration is useful in many applications ranging from measurement of hydrogen in the hydrogen economy, explosive atmospheres in safety critical applications to portable medical breath analyses (e.g. Detecting sugar intolerances at point of care.) [1]

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Traditional thin film gas sensors are often produced using gas phase techniques requiring high temperatures or exotic processes meaning that creation of gas sensors can be a relatively expensive process. Wet chemical precursor nanomaterial synthesis often with a relatively low temperature anneal step allow for cheaper sensors to be produced on a greater variety of substrates, in addition these sensors being nanomaterials tend to have large surface to volume ratios allowing for large responses. Typically however low temperature semiconductor gas sensors show characteristically low sensitivities to gases, to improve sensitivities the surface can be decorated with metallic nanoparticles. Being relatively stable, easy to produce and catalytically active noble metal nanoparticles are often used as catalytic agents allowing for lower energy routes and therefore requiring lower temperatures for chemical reactions to proceed. In addition to their chemical activity the metal nanoparticles allow electron transfer between the materials modulating the localized shottky contact induced depletion region.

In this paper highly sensitive hydrogen gas sensors comprising of gold nanoparticle decorated porous zinc oxide nanosheets produced via calcination of layered basic zinc acetate nanosheets have been produced and compared to undecorated porous zinc oxide nanosheet control sensors. The nanosheet precursors (from here on defined as LBZA NS) are produced by a rapid and cheap microwave synthesis previously reported elsewhere [2] and the gold nanoparticles via a relatively well known sodium borohydride (strong reducing agent) reduction with size control provided by Polyvinylpyrollidone in the form of stearic hindrance. Whilst bulk metal gold is typically viewed as being unreactive small nanoparticles are highly active catalysts often used in oxidation reactions, for example carbon monoxide oxidation. [3]

1. Methods

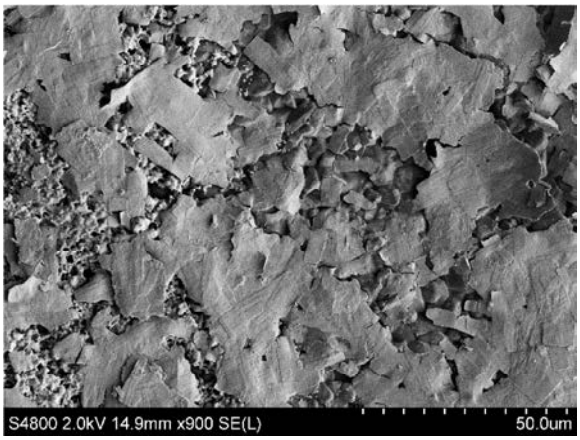
Layered basic zinc acetate nanosheets (Zn5(OH)8(CH3COO)2.2H2O) were produced following a previously reported method [x] by mixing a 60ml solution of 0.1M zinc acetate dihydrate (Zn(CH3COO)2.2H2O) with 0.02M hexamethylenetetramine (HMTA, (CH2)6 N4) in deionized water and microwaving in a standard kitchen microwave at 800W for 1 minute. The resulting solution was left to cool at which point the solution was stirred to briefly suspend the particles and 3ml was transferred to a 15ml centrifuge tube. The solution was centrifuged 5 times removing the supernatant and replacing it with deionized water each time. After the final centrifuge run the solids were topped up to 3ml, vortexed and left in an ultrasonic bath for 2 minutes to allow any clumps to be redispersed. The gold nanoparticles were produced by pipetting 1ml of a solution containing 1mg of dissolved 1.2 MDa polyvinylpyrollidone (PVP) and 1mg sodium borohydride into 1ml of 6.35mM hydrogen tetrachloroaurate in deionized water and vortexing. Upon addition of the sodium borohydride an instant colour change to dark blood red can be observed. To form the gold nanoparticle decorated nanosheets 200µL of the gold nanoparticle solution is added to the 3ml of cleaned sheet solution (corresponding to a total gold loading post annealing of approximately 2.1% wt.) and vortexed until the solution is clear and the solids have turned red. The solution was centrifuged once to remove the vast majority of the salts in solution and then 100uL was drop cast onto an aluminium oxide substrate with platinum IDE electrodes and heater track, followed by annealing at 350C for 30 minutes. Control sensors were produced in the same way without the addition of the gold and subsequent centrifuge step.

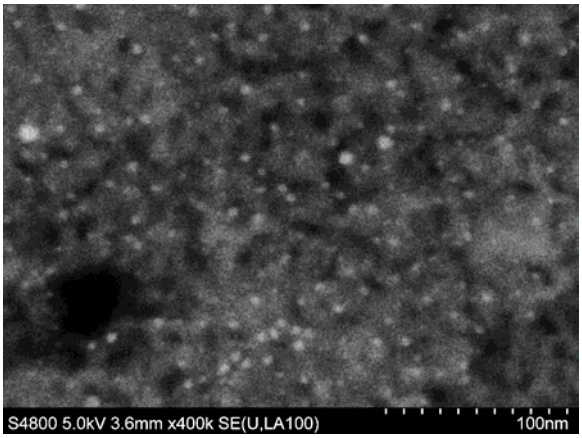
Morphology of the nanoparticles was investigated using a Hitachi S4800 Type II FEGSEM with in chamber ExB filter to allow energy filtered qualitative elemental density analysis.

The sensing response of the sensors under gas flow was tested using a homemade automated gas sensing rig, under 320 Sccm Nitrogen, 80 sccm N5 purity Oxygen during dry air background/ purge steps and 80 sccm oxygen and varying ratios of Nitrogen and 1000ppm Hydrogen balanced with Nitrogen with a total flow of 320 sccm during the test steps. During the concentration response tests the nitrogen and nitrogen balance flow rates were adjusted in a staircase fashion with the hydrogen flow increasing each step. The temperature was controlled via heater tracks on the reverse side of the substrate and the current of the sensing layer was measured using a Keithley 6487 picoammeter under a 10V bias.

2. Results

3.1 SEM Analysis of strucures





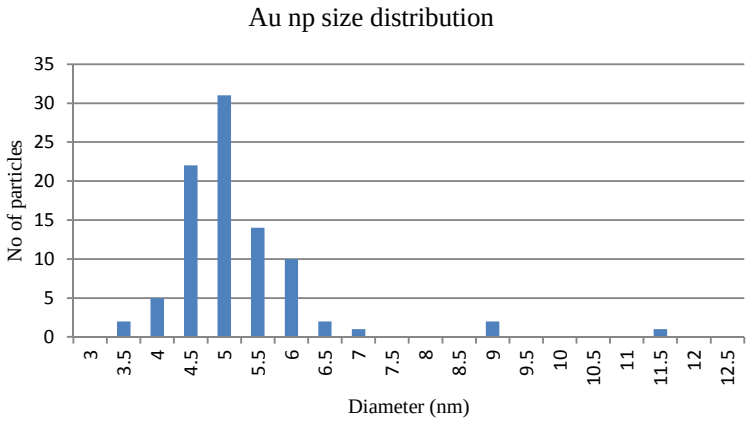


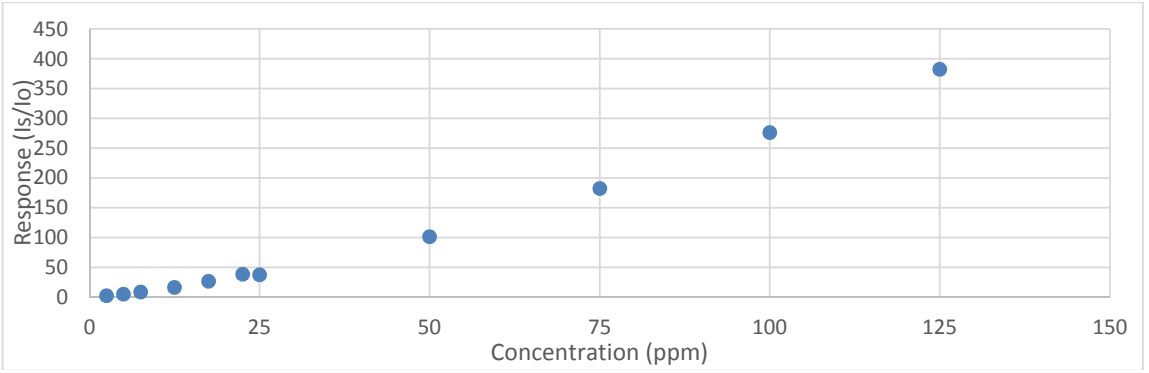
Figure 1 (top left): Zinc oxide nanosheets covering platinum electrodes (bright, left) aluminium oxide (dull grains, right.) Figure 2 (top right): 5nm gold nanoparticles on zinc oxide grains. Images captured using a Hitachi S4800 FEG SEM. Figure 3 (below): Histogram of Au np diameter distribution.

The unannealed LBZA NS clearly have a rectangular morphology with a dispersed size range, though normally under 30µm in length, previous investigations in to the material [2] utilising AFM have revealed heights typically around 80nm. Post annealing the sheets tend to break up as the organic component decomposes creating a nanogranular texture as can be seen in the dark grey structure in fig 2. The gold nanoparticles as seen in Fig. 2 (bright particles), have a mean diameter of approximately 5nm with a standard deviation of 1.1 nm, from the size distribution in figure 3 it can be seen that, with practically all nanoparticles being 7nm or smaller.

3.2 Gas response

The gold catalysed sensor shows a strong response to hydrogen, being able to double the current flowing at hydrogen concentrations as low as 2.5ppm and to produce a current gain of 382.45 at 125ppm. Comparatively even at 300C the control sensor produced a current gain of only 1.54. To test dynamic range at low temperatures the

sensor temperature was set to 200 C, Fig 4 shows the concentration curve. The currents produced under testing range from tens of nanoamps to greater than 60 microamps.



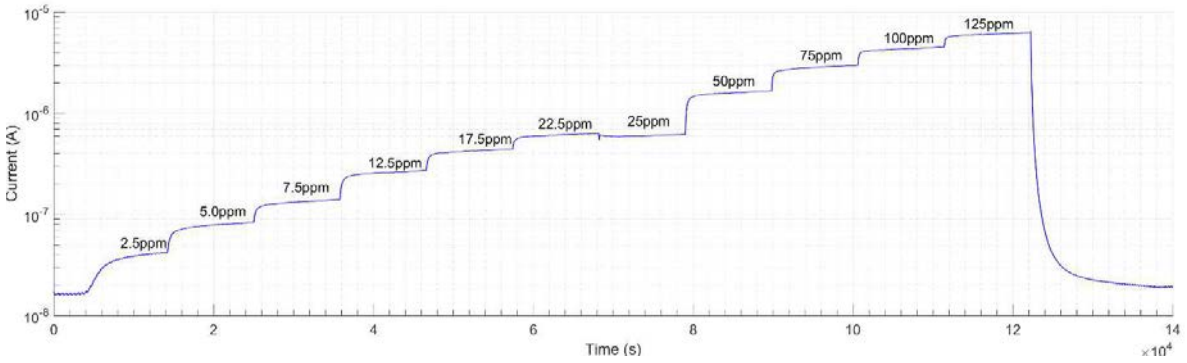


Figure 4 (Top): Concentration vs Response. Response defined as the background normalised current gain, i.e. Response = I signal equilibrium (Is)/ I background(Io). Figure 5 (bottom): Current vs time for incremental flow of hydrogen. Drop in signal between 22.5ppm and 25ppm due to test gas MFC range switch, response and flows are within 1% full scale error of MFC.

4. Conclusion

Highly sensitive gold nanoparticle catalytically active hydrogen sensors have been produced by simple, rapid and cheap synthesis methods, with a current gain of 382.45 to 125 ppm hydrogen at 200 C utilising relatively low gold loadings (2.1 % weight.) The large current response (10s of µAs) at lower concentrations realistically allows use in portable devices e.g. in point of care medical equipment. In addition the simplicity and rapidity of the methods involved allow the possibility for scale up using printing and coating processes.

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